## ELECTROCHEMICAL DETERMINATION OF THE METAL COMPLEXING CAPACITY

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Metal complexing capacity (MCC) is the parameter of a seawater which shows in the indirect way the amount of ligands which form inert complexes with particular heavy metal and can be of interest in characterization of the purity of seawater. Its determination needs a measuring procedure and a data treatment, which will be discussed (RUZIC, 1982) and shown in Figure 1.

discussed (RUZIC, 1982) and shown in Figure 1. Depending on the working electrode used, we distinguish two procedures, first using static mercury drop electrode (SMDE) assembly and the second using thin mercury film glassy carbon disk electrode (TMFGCDE) assembly (OMANOVIC et al., 1994).

Concerning SMDE assembly, from cathodic measurements in 2-3 orders of magnitude higher concentration range than found in natural seawater samples ( $5 \times 10^{-5}$  mol  $1^{-1}$ ) with model solutions with copper (II) and ethylenediamine-tetraacetic acid (EDTA), it is concluded that MCC determination would not be possible because peaks of free and labile complexed copper and the inert one are so close that no deposition potential was available where only the free copper would be reduced and accumulated for ASV technique which is necessary in low concentration range. Triton-X-100 (T-X-100) separates the waves of free and inert complexed copper. In order to find the best conditions for Cu CC determination, dependencies of Cu oxidation peak current height as well as Cu EDTA reduction potential have been measured. Also the linearity of standard additions of copper in presence of T-X-100 is checked.

Concerning TMFGCDE assembly, from cathodic measurements, it has been noticed that the separation of mentioned waves, was dependent on the thickness of the mercury film. When the film is thicker, these two waves are closer, approaching to the signals corresponding to the mercury drop electrode.

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When comparing the TMFGCDE with the SMDE regarding MCC determination, we have to point out that TMFGCDE has the detection limit an order of magnitude lower. As a procedure it is simpler and needs no addition of chemicals to the sample. Because of the better stirring possibilities, the double layer is thinner which enables better distinguishing between labile and inert complexes and in that sense better MCC determination.

The limitations of that electrode assembly caused by cell wall adsorption will be presented. Advantages of SMDE are the renewal of the electrode surface which is important in the presence of strong surface active substances.



Figure 1. a) A pseudopolarogram of 3 x 10<sup>-7</sup> M copper (II) in 0.55 M NaCl in the presence of 2 x 10<sup>-7</sup> M EDTA. b) Metal complexing capacity determination

## REFERENCES

I. RUZIC, 1982. Theoretical aspects of the direct titration of natural waters and its information yields for trace metal speciation, *Anal. Chim. Acta*, 140 99-113.
D. OMANOVIC, Z. PEHAREC, T. MAGJER, M. LOVRIC and M. BRANICA, 1994. Wall-jet electrode system for anodic stripping voltammetry. *Electroanalysis*, in press.

## A PRELIMINARY STUDY ON THE NUTRIENTS IN THE AL-KABIR AL-SHIMALI RIVER ESTUARY (SYRIA)

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In spite of the presence of several, permanent and seasonal, rivers in the Syrian coastal region, there is not, as far as we know, any study on their different hydrochemical properties, especially concerning the seasonal variations of nutrients in the estuarine waters, and their effect on the marine coastal ecosystems. Al-Kabir Al-Shimali river is the longest Syrian coastal river (96 km.); its estuary is situated in the south of Lattakia city. The tidal regime of the Al-Kabir Al-Shimali river estuary (KSRE) is low, as it is the case of the Eastern Mediterranean river estuaries, and the intermixing estuarine zone is relatively limited.

This research aims to make a first series of inspections on the nutrients levels in the KSRE, and we hope to develop it later to cover hydrochemical and biological cycle in the KSRE and neighboring coastal waters.

The sampling program is carried out between January 1991 and February 1992. Nutrients were determined in surface waters only. Analyses of nutrients were based on standard spectrophotometric methods (AMINOT & CHAUSSEPIED, 1983). The indophenol blue technique was used for ammonium determination, while nitrite and nitrate were analyzed as a pink azo compound before and after reduction of the samples on cadmium columns treated with copper sulfate. Orthophosphates (reactive phosphorus) were determined by molybdenum-blue technic. Salinity and temperature were measured in situ with a S-C-T-meter (YSI-33); an ulterior measurement of salinity were performed by titrametric method of Knudsen.

The salinity, of the studied estuarine waters, were ranged between 0.0 and 23%, and the temperature between 8 and 31°C for the whole annual cycle. Nitrates are the more abundant nitrogenous nutrient (1.7 to 37.8 umol/l), and they have the wider seasonal variations. Ammonia concentrations ranges between 0.3 and 5.2 umol/l. Nitrite concentrations were below 1.2 umol/l. The concentration of orthophosphates is usually smaller than 1.7 umol/l. The concentrations of all nutrients decrease in the sea outside the river estuary.

Nutrients concentrations, which studied in the KSRE waters, showed very different variations according to the season and to the considered nutrient (Figure 1). Nitrates and orthophosphates were highest in winter and decreased in spring and summer. Ammonium and nitrites show relatively important concentrations in summer also, after a distinct decrease in April 1991.

The behaviour of nutrients in the intermixing estuarine zone, as it concerns their seasonal variations, and the biological activity of the estuarine ecosystem. The main tendency is accumulation during winter and removal during summer.



Figure 1: Seasonal variations of nutrients, salinity and temperature in the Al-Kabir Al-Shimali river estuarine waters.

## REFERENCES

AMINOT A. & CHAUSSEPIED M., 1983, Manuel des analyses chimiques en milieu marin., CNEXO, Brest, BNDO/Document., 393p.